PREPARATION, CHARACTERIZATION AND APPLICATION OF LIGNIN GRAFT COPOLYMER AS A DRILLING MUD ADDITIVE

by

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LIST OF ABBREVIATIONS

AA	Acrylic acid
ABM	Air and foam-based drilling mud
API	American Petroleum Institute
CMC-HV	High viscosity Sodium Carboxy Methyl Cellulose
cp	Centipoise
DSC	Deferential Scanning Calorimetry
EFB	Empty fruit bunch
FTIR	Fourier Transform Infrared Spectroscopy
lb/100 ft^2	Pound per 100 square foot
GG	Guar Gum
KBr	Potassium bromide
KL	Kraft lignin
LGC	Lignin graft copolymer
n	Flow index
OPEFB	Oil palm empty fruit bunch
OBM	Oil-based drilling mud
PTS	p-toluenesolfonicacid
rpm	Revolutions per minute
SEM	Scanning Electron Microscopy
T_c	Crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
TGA	Thermogravimetric (TGA) Analysis

% TC	Percentage of total conversion
WBM	Water-based drilling mud
W_a	Weight of acrylic acid
W_k	Weight of Kraft lignin
W_t	Total weight of lignin graft copolymer
w/w	Weight per weight
v/v	Volume per volume
XG	Xanthane Gum
μ_a	Apparent viscosity
μ_p	Plastic viscosity
τ_y	Yield point
θ	Gel strength

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PERSEDIAAN, PENCIRIAN DAN PENGGUNAAN KOPOLIMER CANTUM LIGNIN SEBAGAI BAHAN TAMBAH LUMPUR GERUDI

ABSTRAK

Kopolimer cantum lignin (LGC) larut air telah disintesis daripada serat tandan kosong kelapa sawit (OPEFB) sebagai sumber biojisim boleh diperbaharui. Sebagai permulaan, lignin Kraft (KL) diekstrak menggunakan sisa pemulpaan Kraft serat OPEFB. Pengekstrakan KL dilakukan menerusi pemendakan asid terhadap likur hitam yang diperoleh daripada proses pemulpaan Kraft. KL kemudiannya dicantumkan dengan asid akrilik (AA) menggunakan asid p-toluenasulfonik (PTS) sebagai mangkin dalam proses kondensasi melalui teknik pukal. Kopolimer yang terhasil terciri menggunakan kespektroskopan infra-merah jelmaan Fourier (FTIR), permeteran kalori imbasan kebezaan (DSC), permeteran graviti haba (TGA). Spektrum FTIR produk menunjukkan berlakunya penyerapan berikutan wujudnya ikatan ester sebagai bukti cantuman. Keputusan DSC dan TGA menunjukkan peningkatan sifat-sifat terma yang ketara dengan sekurang-kurangnya 27.3%, seiring dengan degradasi rintangan terma. Mikrograf SEM mempamerkan tindak balas percantuman yang telah menghomogenkan struktur morfologi KL. Dalam bahagian aplikasi, LGC dikenakan keadaan simulasi hidrokarbon untuk menguji keupayaannya bertindak sebagai bahan tambah pelbagai fungsi. Lignin yang tercangkuk menunjukkan keupayaan melikat dan pengegelan yang tinggi pada suhu yang tinggi. Ia juga setanding dengan bahan tambah lumpur gerudi komersial yang berada di pasaran.

PREPARATION, CHARACTERIZATION AND APPLICATION OF LIGNIN GRAFT COPOLYMER AS A DRILLING MUD ADDITIVE

ABSTRACT

Water soluble lignin graft copolymer (LGC) was prepared from oil palm empty fruit bunch (OPEFB) fiber as a renewable biomass source. Beforehand, Kraft lignin (KL) was extracted by exploiting the OPEFB fiber Kraft pulping residue. The KL extraction was accomplished through the acid precipitation of black liquor which was obtained from the Kraft pulping process. KL was then grafted with acrylic acid (AA) by using p-toluenesulfonic acid (PTS) as a catalyst in the condensation process via bulk technique. The resulting copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The FTIR spectrum of the product showed absorption due to the presence of ester bonds as a proof of grafting. The DSC and TGA results showed significant improvement in KL thermal properties of at least 27.3% as well as thermal degradation resistance. SEM micrographs illustrated the grafting reaction homogenizing the KL morphological structure. In the application part, LGC has been subjected to the simulated hydrocarbon drilling conditions in order to evaluate its ability as a drilling mud multi-functional additive. The grafted lignin depicts high potential in viscosifying and gelling abilities at high temperature and it is comparable with commercial drilling mud additives available in the market.

CHAPTER ONE

INTRODUCTION

1.1 Lignin

1.1.1 General Description of Lignin

Lignin is a macromolecular biopolymer of vascular plants whose structural composition and environmental reactivity has been the subject of countless articles over the last century. In general, lignin occurs together with cellulose and other polysaccharides in the cell walls of the plants, particularly in woody plants where lignin accumulates between the cellulose microfibrils in the middle lamella and the primary and secondary walls of the xylem elements as shown in Figure 1.1 (Donaldson, 1994; Sharma *et al.*, 2004). In addition, the term lignin is derived from the Latin word *lignum* which means wood; given that, it is the substance that makes trees woody and is present mostly in cell walls of the vascular plants (Rohella *et al.*, 1997).

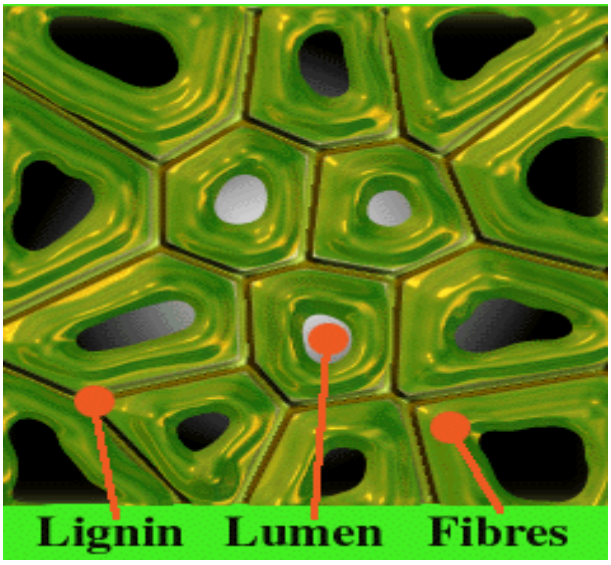

Figure 1.1 Position of lignin inside vascular plants

However, in its native state or as found in plants, it is important to the life of vascular plants (Chakar and Ragauskas, 2004). In this regard, lignin is a main constituent of the cell walls of vascular plants, especially in woody tissues where it is present in high amounts, it acts as a binding agent which provides compressive strength and bending stiffness (Holmgren *et al.*, 2009).

The lignin is an amorphous phenolic complex which is the second in abundance after cellulose; its account for approximately 30% of aromatic biopolymers that represent in the plant biomass (Lapierre *et al.*, 2000). Besides that, lignin plays a crucial part of several properties which make this biopolymer relatively unique in nature. Within this context, the functional significance of lignin has been until now mainly associated with mechanical support of plant organs, improved sap conduction through lignified vascular elements, efficient water transport between cell walls, and the resistance of thermal degradation and fungi attack by defence mechanisms (Boudet, 2000). Other prospective functions have also been investigated, such as the control of cell wall extension via the lignifications of the primary cell walls which are in a dynamic state of extension and concomitant apposition of new wall layers (Müse *et al.*, 1997).

1.1.2 Structure of Lignin

The structure of lignin has been studied extensively by a variety of methods, including analytical and degradative methods as well as the parallel examination of the reactions of lignin and model compounds (Erdtman, 1957). Earlier studies have been reported that, as shown in Figure 1.2, lignin has a complex phenolic polymeric structure which results from the condensation of phenylpropane units, i.e. monolignols (Partenheimer, 2009). In spite of that, the structure of lignin varies

depending on its origin and the extraction method that was applied to obtain it (Toledano *et al.*, 2010). Figure 1.2 shows a proposed structure of softwood lignin (Sun *et al.*, 1997). In view of that fact and since all lignins show a certain variation in their chemical structure, it is difficult to determine the specific structure of lignin as a chemical molecule.

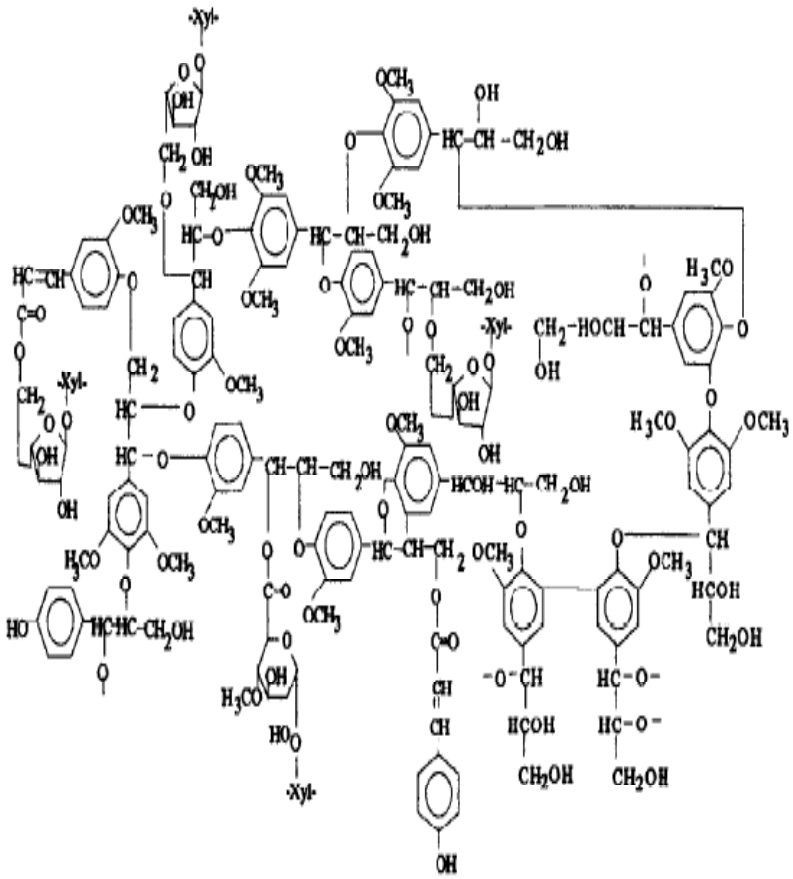

Figure 1.2 A proposed structure of softwood lignin

Apart from that, in contrast to other biopolymers which consist of a single intermonomeric linkages, the tight physical binding and chemical linkages between lignin and cell wall polysaccharides practically prevent its isolation in unaltered form. This also makes it very difficult to use degradative or nondegradative methods

for structural determination of lignin (Holtman *et al.*, 2003). As a consequence, the understanding of the exact structure of lignin, either in natural or after extraction, is concluded as a sum which based on the information that obtained from; studies of lignin biosynthesis mechanisms and the analytical data of the extracted lignin.

However, lignin is a network polymer that results from the dehydrogenative radical polymerisation of monolignols (e.g. p-coumaryl, coniferyl, and sinapyl alcohols) as illustrated in Figure 1.3. These monolignols are connected via carbon-carbon and ether linkages (Boeriu *et al*., 2004). Furthermore, the relative amounts of the monolignol units differ considerably between plants. In softwood lignin, the type of lignin that is used in this study, the network is formed primarily by coniferyl moieties (95%). The rest consists of p-coumaryl alcohol-type units and only traces amounts of sinapyl alcohol moieties. In hardwood and dicotyl crops like hemp and flax, various ratios of coniferyl/sinapyl have been reported (Dence and Lin, 1992).

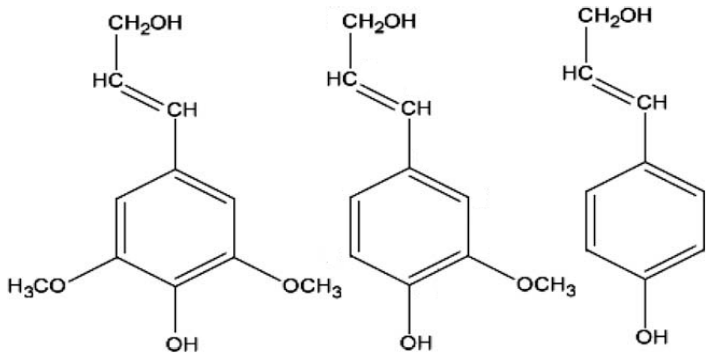

Figure 1.3 Structure of lignin monolignols; (1): p-coumaryl alcohol, (2): coniferyl alcohol, and (3): sinapyl alcohol

1.1.3 Types of Lignin

There are many types of lignin which are classified in terms of different considerations: the chemical structure, the degree of crosslinking, and the age of the plant which lignin is isolated from, the type of plant (hard wood, softwood, grasses, etc.), the pulping process, and the extraction methods. In this regard, the lignin composition will be different not only between plants of different genetic origin, but also between different tissues of an individual plant. Apart from that, the major chemical functional groups in lignin include hydroxyl, methoxyl, carbonyl, and carboxyl groups present in various amounts and proportions, depending on genetic origin and applied extraction processes (Gosselink *et al.*, 2004). In general, commercial lignin is extracted from the pulping waste liquor, i.e. black liquor which is collected after the accomplishment of the pulping process. Additionally, different types of lignin have been described depending on the variation of the employed pulping technology. In details, commercial lignin is divided into two principle categories. The first category comprises conventional or sulfur-containing lignins, which include Kraft lignin and lignosulfonates. These products have been available for many years. Lignosulfonate can be found in large quantities (around 1 million tonnes of solids per year), and Kraft lignins are found in more moderate quantities (around 100,000 tonnes of solids per year) (Gosselink *et al.*, 2004). Conventional lignins used industrially are mainly obtained from softwoods. The second category comprises non-sulfur lignins obtained from many different processes, most of which are not yet commercially implemented: soda lignins, organosolv lignins, steam explosion lignins, hydrolysis lignins (mainly from biofuel production), and oxygen delignification lignins (Mansouri and Salvadó, 2006). In the latter category, due to the lack of suitable industrial process and severely market penetration, only the soda

lignins have the potential to be a more readily available source of such lignins (Lora and Glasser, 2002).

1.1.4 Potential Industrial Applications of Lignin

Traditionally lignin has been viewed as a waste material or a low value by-product of pulping and paper industry with its utilization predominantly limited to its use as a fuel to fire the pulping boilers (Stewart, 2008). Almost all lignins extracted from lignocellulosic materials from the pulp and paper industry are burnt to generate energy and considered as an excellent fuel, since lignin yields more energy when burnt than cellulose. Nevertheless, the possible development in the lignin industrial utilization is limited to very low growth because until now only a small amount (2%) of lignin is commercially used (Gosselink *et al*., 2004). This includes the manufacturing of wide range of products. In fact, due to the lack of appropriate industrial processes, lignin is considered as a mostly non-commercialized product.

On the other hand, lignins have many specifications (chemical and biophysical properties) which can advantageously be exploited to develop new and environmentally friendly products. In this regard, lignins are non toxic, potentially of high value, inexpensive, and available in large amounts. They possess highly reactive locations that can be surprisingly modified through a selection of chemical, physical and/or enzymatic reactions, which give them a great potential for their exploitation as industrial raw materials (Sena-Martins *et al.*, 2008). Industry first began to use lignins in the 1880s when lignosulfonates were used in leather tanning and dye baths (Vinardell *et al.*, 2008). Since then, lignosulfonates have found many applications. Among these applications are: as dispersant in high performance cement applications, water treatment formulations, and textile dyes. Furthermore, they are

used as additives in specialty hydrocarbon drilling well operations and agricultural chemicals. Their other uses are as raw materials in the production of several chemicals namely vanillin, dimethyl sulfoxide (DMSO), ethanol, xylitol sugar, and humic acid. Besides, it is also used as an environmentally sustainable dust suppression agent for roads. Last but not least, lignosulfonates were used in food products, serving as emulsifiers in animal feed. Interestingly, the usefulness of commercial lignosulfonates product comes from their dispersing, binding, complexing, and emulsifying properties (Vinardell *et al.*, 2008). Accordingly, modified lignin has been widely used in different aspects of industries around the world, such as animal bypass protein, gypsum board additives, automotive brakes, wood panel products, phenolic resins, biodispersants, polyurethane foams, epoxy resins for printed circuit boards and surfactants, dyestuff, agro chemicals, and water treatment dispersants (Liu *et al.*, 2008). In the same direction, the long term purpose of this study is to explore the possibility of using the bulk polymerization technique to modify the lignin to be used a mud additive in oilwell drilling operations especially in high temperature and high pressure conditions.

1.1.5 Source of Lignin in This Study

In recent years, oil palm empty fruit bunch (OPEFB) fiber (Figure 1.4), which is one of the lignocellulosic materials (biomass), shows great potential to be used as raw material in the Kraft pulping process, especially in Malaysia, which is one of the major palm oil producers in the world (Ibrahim *et al.*, 2005). In conformity with that, Kraft black liquor remained as a waste after the completion of the pulping process. This aquatic colored and toxic effluent (Gupta *et al.*, 2007), i.e. black liquor, was considered as a serious pollution source and has caused costly disposal problems

(Malaviya and Rathore, 2007). Kraft black liquor consists of dissolved biomass materials, such as lignin, hemicellulose and degradation products of cellulose and hemicellulose (sugar acids) (Wallberg *et al.*, 2006). Such industrial waste products could be a feasibly cheap and available abundantly to produce adsorbent, corrosion inhibitor, and chemically modified biopolymer (Gupta *et al.*, 2003). In agreement with that, this study was an effort to produce a chemically modified biopolymer (lignin graft copolymer) using Kraft lignin as a raw material. The Kraft lignin was extracted from the Kraft black liquor via acidification process using sulfuric acid.

Figure 1.4 Oil palm empty fruit bunch (OPEFB) fiber

1.2 Oil Palm

1.2.1 Oil Palm Industry

Oil palm is a tree whose fruits are used for the extraction of edible oil. It originated from West Africa, cultivated in all tropical areas of the world and has become one of the main industrial crops (Kelly-Yong *et al.*, 2007). Additionally, the

oil palms (*Elaeis*) comprise two species of the *Arecaceae*, or palm family. The African Oil Palm *Elaeis guineensis* is native to west Africa, occurring between Angola and Gambia, while the American Oil Palm *Elaeis oleifera* is native to tropical Central America and South America. The generic name is derived from the Greek for oil, *elaion*, while the species name refers to its country of origin. They are used in commercial agriculture in the production of palm oil.

In Malaysia, the oil palm, *Elaeis guineensis*, is a tropical palm tree, therefore it can be cultivated easily in Malaysia. In addition, the oil palm tree in Malaysia originated from West Africa where it was growing wild and later it developed into an agricultural crop. It was introduced to Malaysia in 1870 as an ornamental plant, and in 1917, the first commercial planting was undertaken (Abbas *et al.*, 2006). The growth of the industry has been phenomenal and Malaysia is now the largest producer and exporter of palm oil in the world, accounting for 52% or 26.3 million tonnes of the total world oils and fats exports in year 2006 (Sumathi *et al.*, 2008).

1.2.2 Oil Palm Biomass

Besides producing palm oil, Malaysian palm oil industry also generates huge quantity of oil palm biomass including oil palm trunks, oil palm fronds, empty fruit bunches (EFB), shells and fibers. There was annual generation of 9.66, 5.20 and 17.08 million tonnes of fiber, shell and empty fruit bunches, respectively, in the year 2005 in Malaysia (Chew and Bhatia, 2008). In view of that, with the projected growth in the cultivation of oil palm, the destination of the tremendous amount of residues raises concerns (Kelly-Yong *et al.*, 2007). As the oils form about 10% of the total dry biomass produced by the palm, the other 90% of the biomass represents a further huge source of fiber and cellulosic materials which await further commercial

exploitation (Basiron, 2007). Presently, most of this waste is incinerated to generate energy, which leads to serious environmental problems, such as earth warming due to emission of CO_2 (Masuda *et al.*, 2001). On the other hand, this waste (oil palm biomass) has a potentiality to be converted to commercial products, such as wood pulping raw material, animal food, fertilizer, and absorbent. It can also be converted to bio-fuel such as bio-ethanol or can be used to generate electricity (Shuit *et al.*, 2009). Generally, the oil palm biomass consists of cellulose, hemicellulose, and lignin, and the content of the components varies depending on plant species (Peters, 2007). With continuing efforts that made possible the utilization of the oil palm biomass in many industrial aspects, this study investigated the possibility of using oil palm biomass as a drilling mud additive in oil and gas drilling industry.

1.3 Drilling Mud and Drilling Mud Additives

1.3.1 Drilling Mud

During the drilling of an oil or gas well by means of rotary drilling tools, drilling mud is circulated down hole through a drill string and flows back to the surface through the annular space between the drill string and the borehole. This circulation (Figure 1.5) is to achieve specific functions which include providing a sufficient hydrostatic pressure to prevent influx of formation fluids, coding the drill bit, carrying out drill cuttings, and suspending the drill cuttings while drilling is paused or the drilling assembly is brought in and out of the hole (Espinosa-Paredes and Garcia-Gutierrez, 2004). Interestingly, the cost of drilling mud and drilling mud additives is typically about 10% (may vary greatly) of the total cost of well cost. Therefore, better management and development of drilling mud and drilling mud additives could effectively economize the drilling operations.

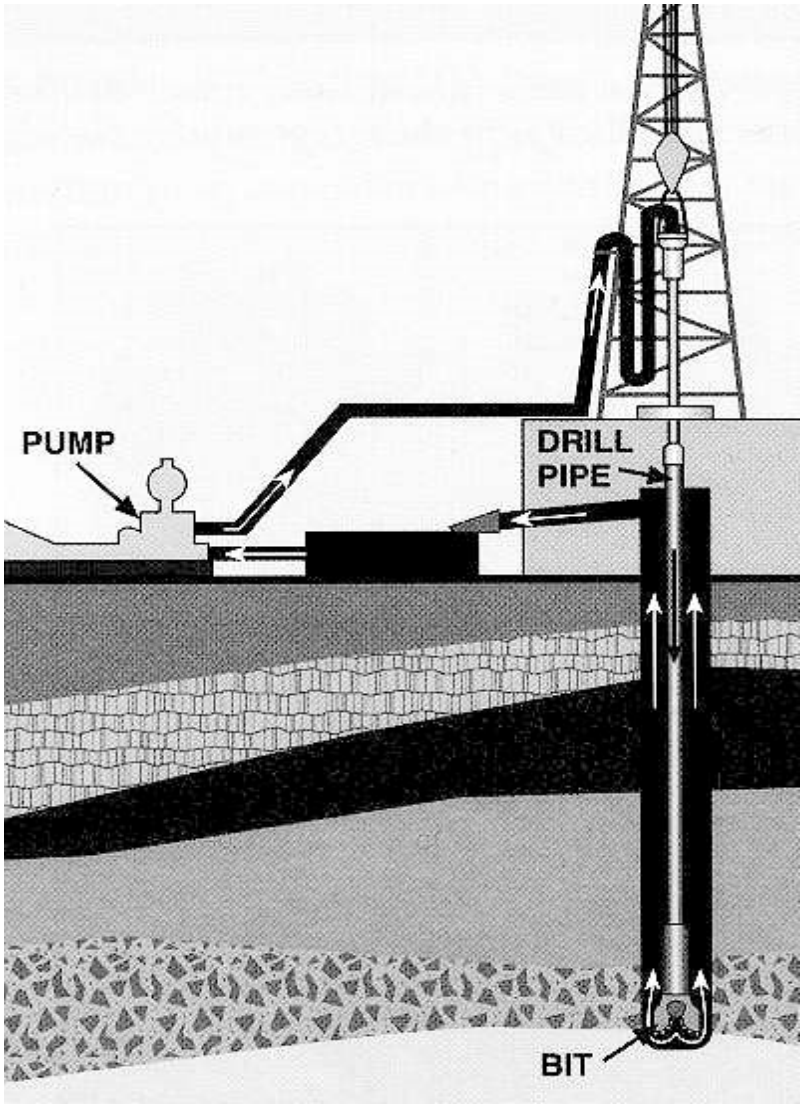

Figure 1.5 The circulation of drilling mud

1.3.2 Types of Drilling Mud

The selection of proper drilling mud during the rotary drilling process is vital for the success of any drilling operation. In fact, most drilling problems are a direct or indirect consequence of improper mud selection. Within this context, there are many types of drilling mud used in the petroleum industry. Generally all of these types are classified into three main categories: (1) air and foam-based mud (ABM); there are drilling conditions under which a liquid drilling fluid is not the most

desirable circulating medium. In such a case, air or foam is used as drilling mud to accommodate these special conditions. Moreover, this is the most advantageous and effective type of drilling mud in consolidated rock formations, (2) oil-based mud (OBM); this drilling mud is made up of oil as the continuous phase. Diesel oil is widely used to provide the oil phase. In addition, this type of drilling mud is more expensive, as it requires stringent pollution control measurement and is also difficult to dispose, and (3) water-based mud (WBM); this type is the mud in which water is the continuous phase. This is the most common drilling mud used in oil drilling and it consists mainly of water, clay, and specialized chemical additives. Besides that, this type is mixed friendly with water and allows drilling mud additives to perform efficiently, beyond that, it is inexpensive and presented less environmental problems compared to oil-based mud (Hamida *et al.*, 2009). Owing to that fact, the type of drilling mud used in this study is the water-based mud.

1.3.3 Drilling Mud Additives

In the course of drilling an oil or gas well, the drilling mud without any additives, is unable to provide satisfactory rheological properties required for optimum performance in well drilling (Mahto and Sharma, 2004). Thus, a number of additives are used to alter the mud properties to fulfill all of the requirements of drilling mud. In addition, different types of additives, either chemicals or polymers, are used in designing a drilling mud to meet some functional requirements, such as appropriate mud rheology, density, mud activity, fluid loss control, etc. These additives are divided into different types based on drilling mud basic properties, such as viscosity, density, gel strength, and filtration. These types include (Caenn and Chillingar, 1996):

- Thinners: this type of additives are used to reduce the viscosity of the drilling mud and it is serves as deflocculant and dispersant. Such additives included lignosulphonate, chrome lignosulphonate, sodium tertaphosphate, and sodium acid phosphate.
- Thickeners (viscosifiers and gelling agents): they are additives used to increase the drilling mud viscosities and gel strength at low concentrations. Among these additives are bentonite, xanthan gum, carboxymethyl cellulose, and guar gum.
- Fluid loss controlling agents: filtrate or fluid loss reducers serve to decrease fluid loss. The drilling mud fluid loss property is a measure of the liquid phase tendency to pass through the filter cake. Examples of this type include names such as polyacrylates, starch, and carboxymethyl starch.
- pH controlling agents: these additives are employed to control the pH of the drilling mud in order to avoid the corrosivity of the drilling tools. They are also applied to prevent the occurrence of drilling mud flocculation. Such additives are caustic soda, ash soda, and acetic acid.
- Weighting agents: these materials are used to control formation pressures, check formation caving, and facilitate pulling dry pipe. They included barite, iron oxides, and calcium carbonate.

It is noteworthy, when drilling in deep wells for oil, gas or geothermal reservoirs, high temperatures are usually encountered which adversely influence the performance of drilling muds (Kelessidis *et al.*, 2007). Also, a major difficulty in formulating high-temperature drilling muds is that mud is negatively affected by elevated temperatures, first gelling excessively and then becoming inert at extreme

temperatures (Caenn and Chillingar, 1996). For that reason, there is always a need for drilling mud additives which can stabilize drilling mud suspensions at high temperatures. This need can be fulfilled by developing new additives that have better resistance to the high temperature drilling operations. In the same way, some parts of this study were designed to overcome such cases. In this regard, the lignin chemically modification process by means of graft copolymerization technique could offer such kind of additives, i.e. thermally stable drilling mud viscosifiers and gelling agents.

1.4 Previous Lignin Graft Copolymerization Studies

Various studies have been conducted on lignin in order to overcome biomass environmental problems and produce new products with beneficial properties. One of these studies is graft copolymerization of lignin to produce a copolymer used as drilling mud thinner and viscosity reducer in high temperature (Wei *et al.*, 2002). Another graft copolymerization reaction of lignin with 1-ethenylbenzene was used efficiently to enhance thermal stability as well as to change the hydrodynamic radius of poly (1-phenylethylene) (Chen *et al.*, 1996). Graft copolymerization reaction of lignin by means of a specific monomers can be conducted either by the addition or condensation copolymerization. Apart from that, the addition copolymerization reaction is normally carried out using either free radicals or the ionic copolymerization process. Accordingly, a variety of vinyl monomers has been successfully grafted on the lignin using free radical copolymerization in appropriate aqueous or organic solvents. The grafting reaction can be initiated by calcium chloride with hydrogen peroxide as a redox initiator which induces the configuration of vinyl homopolymers on the lignin backbone (Chen and Meister, 1999), and then

accelerating the formation of lignin graft copolymer (Bonini *et al.*, 2001). In the same direction, ferrous ion with benzoyl peroxide is used as the initiator to create free radicals of acrylamide on the lignin structure (Mohamad Ibrahim *et al.*, 2006). These techniques are used to design lignin graft copolymer that has been well studied compared to the condensation technique. Remarkably, none of these studies has used p-toluenesolfonicacid (PTS) as a catalyst to accomplish the grafting lignin reaction. In general, the condensation technique can be conducted using a solvent as a reaction medium (i.e. solution copolymerization) and without a solvent (i.e. bulk copolymerization). The bulk condensation technique is conducted in the absence of any solvents that restrict possible a solvent effect. Moreover, the bulk technique only requires simple equipment to run the reaction and hence it is much preferred due to the economical aspect.

1.5 Problem Statement

As a drilling operation proceeds deeper, drilling mud temperature tends to increase rapidly. This increase influences the mud rheological properties negatively. The negative effect of the increase of the temperature includes severe decrease of drilling mud viscosity and gel strength, which makes many of mud additives not functional at high temperature.

On the other hand, efforts are needed to be taken seriously against the large amount of lignocellulosic waste from oil palm industry. Recycling the unwanted materials into a valuable product is an industrial and environmental challenge which necessitates the need of better waste management.

1.6 Objectives of this Study

The objectives of this study were summarized as follows:

1. To optimize the use of lignocellulosic materials from oil palm wastes in the preparation of useful and valuable product, such as a gelling and viscosifying agent for drilling mud.
2. To provide a method for producing a gelling and viscosifying agent for drilling mud which is applicable in high temperature hydrocarbon well.
3. To develop a gelling and viscosifying agent for drilling mud which exhibits good competition with commercial gelling and viscosifying agents.

1.7 Scopes

This study focuses on the preparation of water soluble lignin graft copolymer utilizing the effluent (black liquor) from the Kraft pulping process of the oil palm empty fruit bunch (OPEFB) fiber. Also, it investigates the applicability of lignin graft copolymer as a prospective drilling mud additive in terms of viscosifying agent, gelling agent, and pH controlling agent.

CHAPTER TWO

MATERIALS AND METHODS

This chapter covers the experimental part and the characterization studies which had been accomplished to fulfill the scopes of this study.

2.1 Materials

The raw material used in this study was oil palm empty fruit bunch (OPEFB) long fiber supplied by Sabutek (M) Sdn. Bhd, a Malaysian company that specializes in the recycling of OPEFB.

The catalyst p-toluenesulfonic acid (PTS) was used as received from Merck (Merck, Germany). Acrylic acid (AA) with 99% purity was purchased from Aldrich® (Sigma-Aldrich, USA). AA was purified under vacuum distillation process to remove phenolic inhibitors, stored in the refrigerator, and brought to room temperature before being used. The commercial viscosifying and gelling agents, High Viscosity Sodium Carboxy Methyl Cellulose (CMC-HV), Guar Gum (GG), and Xanthane Gum (XG) were supplied by Kota Mineral Chemical (M) Sdn. Bhd, Sim Company and Aldrich® (Sigma-Aldrich, USA).

2.2 Characterizations

2.2.1 Differential Scanning Calorimetry (DSC) Analysis

In this study, glass transition temperature (T_g) values of KL and LGC were estimated using Perkin Elmer model Pyres 1 DSC. Approximately 10 mg of sample was heated from -50°C to 180°C at the heating rate of 20 °C/min in a nitrogen atmosphere at the flow rate of 30 mL/min.

2.2.2 Thermogravimetric Analysis (TGA)

In the present study, TG-FTIR analysis was conducted to investigate the thermal degradation behavior as well as the weight loss rate of KL and LGC. Apart from that, this analysis was carried out using Thermal Analyzer, model TGA/SDTA 851 fitted with Fourier Transform Infrared (Mettler Toledo) in order to analyze the evolved gases that result from the thermal decomposition of samples. The samples were heated from 30°C – 900°C at the heating flow rate of 20°C/min in nitrogen gas at the flow rate of 30 mL/min.

2.2.3 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was used as an analytical technique for the estimation of the functional groups presented in lignin (Boeriu *et al.*, 2004).

In this study, FTIR spectroscopy was able to differentiate the chemical bonds in the molecular structure of KL and LGC. The ungrafted KL and LGC samples were analyzed using KBr pellet technique. In this technique, the KBr thin pellet was prepared by grinding 1% of sample into potassium bromide (KBr). It was then scanned by the Perkin Elmer system 2000 FT-IR spectrometer in the range from 4000 cm^{-1} – 400 cm^{-1}.

2.2.4 Scanning Electron Microscopy (SEM)

In the present study, Kraft lignin (KL) and lignin graft copolymer (LGC) surface layers morphologies were analyzed using scanning electron microscope (SEM) model LEO Supra 50 VP Field Emission. All samples were sputter coated with 20 nm gold layer before being subjected to SEM analysis.

2.3 Solubility Tests

A variety of polar and non-polar solvents as well as diluted acidic solutions were used in the attempt to determine the solubility of KL and LGC. Apart from that, a range of various temperatures were applied with vigorous stirring. Experimentally, 2-5 mg of the sample was placed into 10-20 mL of solvent in a small beaker, after which, the mixture was observed over a period of time.

2.4 Isolation of Kraft Lignin (KL)

This technique includes different laboratory procedures outlined in Figure 2.2. In addition, these procedures have been applied subsequently in order to produce pure KL. Apart from these, they consist of three experimental processes as explained in the following subsections.

2.4.1 Oil Palm Empty Fruit Bunch (OPEFB) Kraft Pulping

The Kraft pulping process involves digesting of OPEFB fibers at elevated temperature and pressure in *cooking liquor*, which is an aqueous solution of sodium sulfide (Na_2S) and sodium hydroxide (NaOH). The cooking liquor chemically dissolves the lignin that binds the cellulose fibers together.

Prior to the pulping process, 1000 g of OPEFB fibers was soaked in water for two days to remove non-fibrous materials. In the pulping process, the soaked OPEFB fibers were mixed with 41.8 g of Na_2S, 128.7 g of NaOH, and 5.6 L of distilled water in a 20 L stainless steel rotary digester. After which, the mixture was heated from approximately 70°C to a maximum cooking temperature 170°C, followed by 3 hr cooking period. Figure 2.1 shows the stainless steel rotary digester. Once the cooking

period was completed, the contents of the digester were transferred to a container and washed in the pulp washer, where the spent cooking liquor (black liquor) was separated from the pulp.

Figure 2.1 Stainless steel rotary digester (pulping machine)

2.4.2 Extraction of Kraft Lignin (KL) from Kraft Black Liquor

The extraction of KL from the black liquor was accomplished by employing an acidification method. In this direction, the high alkali pH black liquor which was collected after the completion of the pulping process was then acidified using sulphuric acid in order to recover KL as precipitate. In particular, 800 mL of black liquor in 1000 mL beaker was gradually treated with few drops of 20% v/v sulphuric acid with simultaneously measuring the pH value until pH 2; thereby a precipitation

of KL was formed. The precipitate was filtered and washed with pH 2 water, which was prepared using the same acid in the previous step. KL was then dried in a vacuum oven at 45°C for 72 hr. In order to avoid the moisture in the KL particles, it was grinded to a powder form and dried again in a vacuum oven at 45°C for 72 hr.

2.4.3 Purification of Kraft Lignin

In general, lignins are rarely isolated as pure materials, and are always associated with carbohydrate linkages (cellulose and hemicellulose) to varying extent depending on their isolation procedure (Singh *et al.*, 2005).

The purification of KL was conducted by extracting KL in the soxhlet apparatus for 6 hr with n-pentane to remove lipophilic, non-lignin matters such as wax and lipids (Sun and Tomkinson, 2001). The precipitate was filtered and washed twice with pH 2 water to remove the excess n-pentane and non-lignin phenolic compounds which may still remain after the pulping process. The purified KL was then dried further in the vacuum oven at 45°C for another 48 hr.

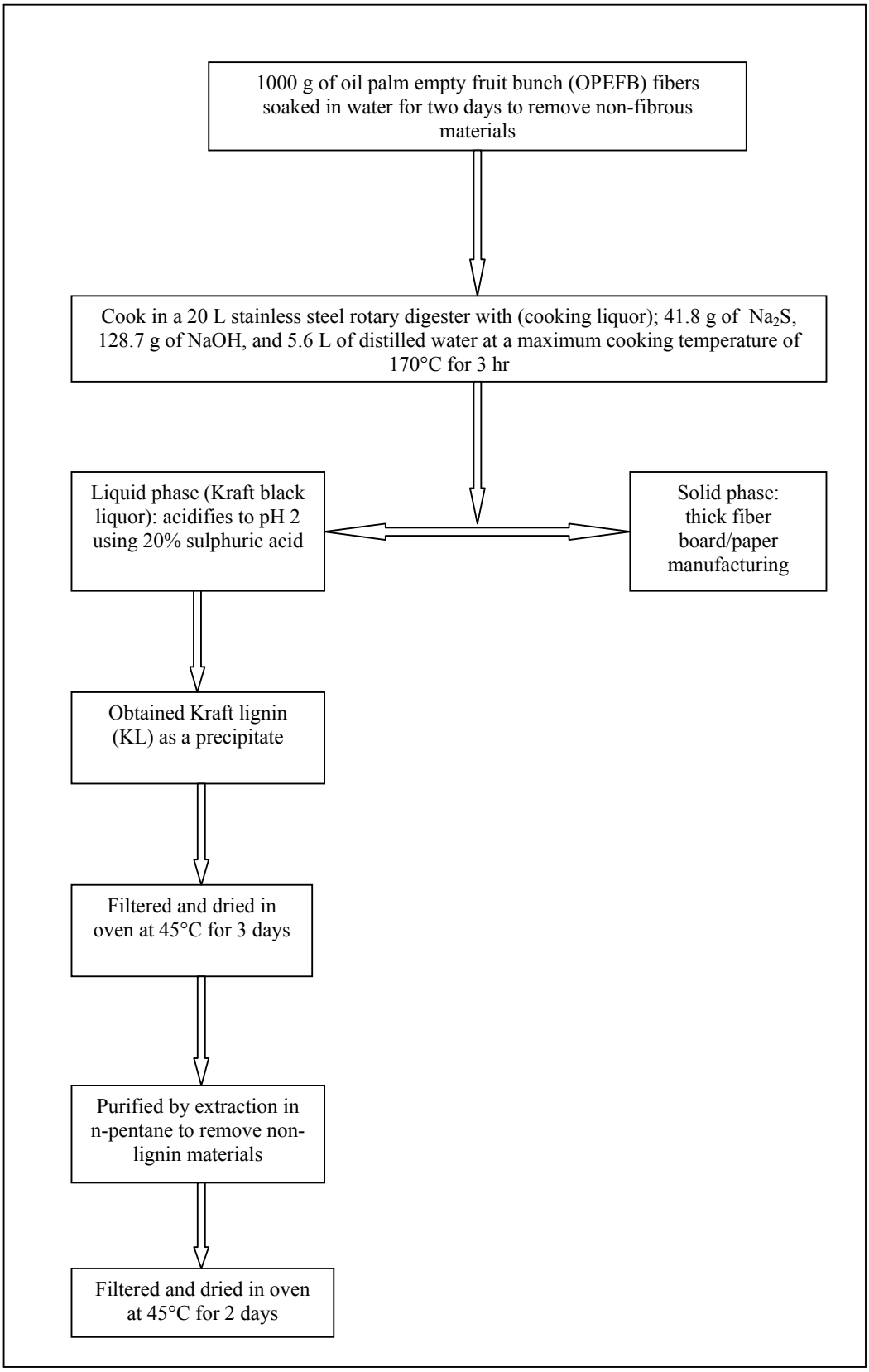

Figure 2.2 Schematic diagram of isolation procedures of Kraft lignin from OPEFB fiber

2.5 Graft Copolymerization Reaction

2.5.1 Synthesis of Lignin Graft Copolymer (LGC)

A grafting reaction was achieved in 5 mL test tubes equipped with magnetic stirrers. Figure 2.3 shows the schematic diagram for the synthesis process of LGC. In details, about 0.75 g of PTS was introduced into each tube with appropriate amounts of Kraft lignin (KL) and acrylic acid (AA). The tubes were deoxygenated by flushing them with nitrogen gas for 10 min, sealed with aluminum foil and then placed in a water bath at 80^{o}C for 18 hr with vigorous stirring. After a specific reaction time, the tubes were immersed in an ice bath at 0^{o}C for one hour with incessant stirring. The result was a highly turbid black liquid that was decanted into 0.1 M zinc sulfate aqueous solution at a ratio of 1:10 v/v with agitation and was allowed to stand at room temperature overnight. After this period, unreacted KL was precipitated and removed by filtration. The light brown liquid was evaporated to remove the aqueous solution and unreacted AA. The lignin graft copolymer (LGC) was obtained as light brown fine particles. These particles were collected and dried in an oven at 100^{o}C for 72 hr to remove moisture from the LGC.

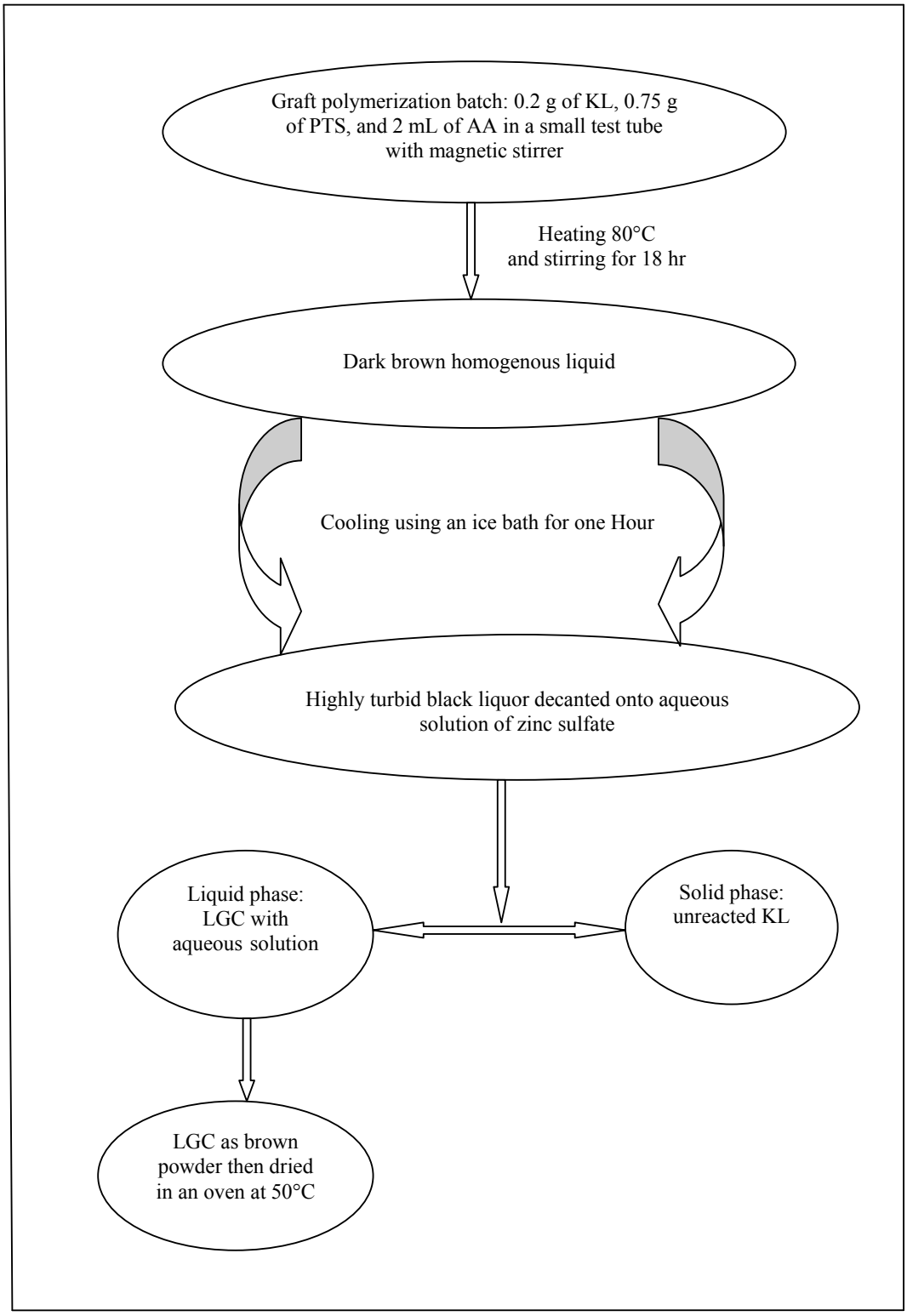

Figure 2.3 Schematic diagram of graft copolymerization reaction of KL